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The Preparation of Stable Colloidal Poly(vinyl alcohol) Composites of Cu_2O and Cu

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Stable colloidal particles of reddish brown Cu_2O–PVA and grayish black Cu–PVA composites have been prepared by the reduction of green Cu^{2+}–PVA complexes in aqueous solutions with hydrazine, at the [hydrazine]/[Cu^{2+}] ratios of 1—3 and 15 or more respectively, where PVA represents poly(vinyl alcohol). The average diameters of the Cu_2O and Cu particles in these composites have been estimated to be about 200 and 300 Å respectively from the half widths of the X-ray diffraction peaks for the corresponding powder samples.

There have been several papers on the preparation of copper sols by the chemical reduction of copper(II) salts in aqueous solutions in the presence and absence of polymer-protecting agents.[1–4] These colloidal dispersions have found interesting applications. Cu^{2+} ions and poly(vinyl alcohol) (PVA) react at $pH \gtrsim 6$ to form green Cu^{2+}–PVA complexes, which have been identified as polynuclear $Cu(OH)_2$ complexes hydrophobically included by PVA.[5,6] In this work, the chemical reduction of these green Cu^{2+}–PVA complexes has been investigated in an effort to obtain some useful materials. The resulting reduction products have been characterized in some detail, with special interest taken in the role of PVA in them.

Experimental

Materials. Hydrolyzed (100%) PVAs with the average molecular weight of 14000 were purchased from the Aldrich Chemical Co. The concentration of PVA in this work was expressed as [PVA polymer residue], in terms of monomeric residues. All the other reagents were of a reagent grade or higher and were used without further purification. Aqueous solutions of green Cu^{2+}–PVA complexes containing 0.20 M PVA and 10 or 20 mM Cu^{2+} ions were prepared by dissolving the required amounts of $CuSO_4 \cdot 5H_2O$ and PVA in aqueous solutions and by then adjusting the pH to 8.0 with NaOH without any buffer (1 M=1 mol dm^{-3}). Chemical reductions of the complexes in aqueous solutions with sodium tetrahydroborate, hydrazine, hydroxylamine, hydroquinone, and ascorbic acid gave variously colored hydrosols. These sols, except those prepared by hydrazine reduction, were not stable in air, resulting in color changes and precipitations within a day. Hydrazine was found to reduce the Cu^{2+}–PVA complexes to differently colored hydrosols according to the value of R_r=[hydrazine]/[Cu^{2+}]. The colors of these hydrosols were reddish brown, bright yellow, and grayish black at the R_r values of 1—3, 4—15, and >15 respectively. Powder samples were obtained from these hydrosols and their original Cu^{2+}–PVA solutions by pouring them into acetone and by washing the resulting precipitates with acetone several times, as in the recovery of PVA powder from its aqueous solutions. Surprisingly, it has been found that these powder samples include microcrystals of Na_2SO_4 as will be seen in the X-ray diffraction measurements; details will be reported elsewhere.[7] Quantitative analyses of the SO_4^{2-} in these samples by means of an ion chromatograph Model HCL-601 (Tosoh Co., Ltd.) showed that 6.5, 6.2, and 6.2% of SO_4^{2-} are included in the powder samples obtained from the Cu^{2+}–PVA solution at R_p=[PVA Polymer residue]/[Cu^{2+}]=20, the reddish brown hydrosol at R_r=1, and the grayish black hydrosol at R_r=20 respectively. These SO_4^{2-} contents remarkably decreased upon dialysis with cellophane membranes. Elemental analyses for the last two powder samples gave similar results near to C 40.5, H 7.8, and Cu 5.5% (determined by atomic-absorption spectroscopy); these results were not yet useful for the identification of these complicated samples. Strictly speaking, the first sample, whose elemental analysis has already been reported,[6] was analogous. After all, elemental analyses of this kind of complicated polymer are a subject for further investigation.

Measurements. X-Ray diffraction measurements of powder samples were carried out by a Geigerflex recording X-ray diffractometer Model D-3F (Rigaku Denki Co., Ltd.). The visible absorption spectra of hydrosols were measured by means of a Hitachi U-2000 spectrophotometer using a 5-mm quartz cell. Far-infrared spectra of powder samples were recorded with a grating infrared spectrophotometer, Model IR-F (Japan Spectroscopic Co., Ltd.). Magnetic-susceptibility measurements of powder samples were carried out at room temperature by the usual Gouy method, where the contents of the copper or copper-ion species required for the calculation of the effective magnetic moments (μ_{eff}) were determined by means of an atomic absorption and flame-emission spectrophotometer Model AA-782 (Nippon Jarrel-Ash Co., Ltd.).

Results and Discussion

Reduction products of copper(II) salts in aqueous solutions are generally unstable in air, even in the presence of poly(*N*-vinyl-2-pyrrolidone) as a protective polymer.[3,4] Interestingly, however, the reduction of the green Cu^{2+}–PVA complexes in aqueous solutions by hydrazine gave stable hydrosols in air. Powder samples prepared as precipitates by pouring these hydrosols into acetone were also stable in air. All the copper or copper-ion species in the hydrosols were included in the powder samples, since such species could not be detected in the filtrates. This fact, together with the extremely high stability of the reduction products in air, indicates that copper or copper-ion species are bound to PVA and, furthermore, that particles of these species may be protectively coated with PVA. This also seems to be responsible for the stable formation of hydrosols. At present, however, the reason why only hydrazine produces this kind of hydrosol is still obscure.

Figure 1 shows the X-ray diffraction patterns of two powder samples. In both patterns, peaks with the following 2θ values are due to Na_2SO_4: 33.8 (33.9), 31.6 (32.1), 29.7 (29.0), 23.4 (23.1), and 19.2 (19.0), where the numbers in parentheses are the values cited from the literature.[8] In addition, the following peaks assignable to Cu_2O and Cu are observed in the A and B patterns respectively:[9,10] 73.6 (73.5), 61.4 (61.3), 52.2 (52.4), 42.2 (42.3), 36.4 (36.4), and 29.7 (29.6) for the A pattern, and 73.8 (73.9), 50.2 (50.3), and 43.0 (43.3) for the B pattern. Accordingly, these results show the formation of Cu_2O and Cu microcrystals in the reddish brown and grayish black powder samples respectively. X-Ray diffraction patterns for the other powder samples obtained from hydrosols at R_r=4—15 were made up by the superposition of the A and B patterns at varying intensity ratios.

The existence of Cu_2O microcrystals in the reddish brown sample was also supported by the observation of a far-infrared absorption at 615 cm^{-1} assignable to $\nu_{Cu\text{-}O}$ in Cu_2O crystals.[11] Figure 2 shows the visible absorption spectra of hydrosols corresponding to the two powder samples in Fig. 1. The absorption maxima at 510 and 590 nm for the reddish brown and grayish black hydrosols are characteristic of Cu_2O and Cu polycrystals respectively.[12]

All the results of the magnetic-susceptibility measurements for the powder samples obtained from hydrosols at various R_r values are summarized in Fig. 3, which shows a plot of the μ_{eff} values of the samples against their R_r values. The μ_{eff} value of the Cu^{2+}-PVA complexes corresponding to R_r=0 is 1.49±0.01 B.M.[6] The errors of the other μ_{eff} values are ±0.05 or so. The fact that μ_{eff}=0 B.M. for the reddish brown samples at R_r=1—3, as is shown in Fig. 3, indicates that the addition of hydrazine at these R_r values completely reduces all the Cu^{2+} ions in the Cu^{2+}-PVA complexes to diamagnetic Cu^+ ions. The μ_{eff} value tends to increase with an increase in R_r in the range of $R_r>3$ and then finally to level off at $R_r>15$. The implication of this final μ_{eff} value of about 0.8 B.M. is now being considered.

It is important to obtain information on the sizes of Cu_2O and Cu particles in the hydrosols or powder samples. We can approximately estimate these sizes from the half widths of the X-ray diffraction peaks, using the Debye equation of $B=0.9\lambda/(t \cos \theta)$,[13] where B, t, and θ are the half width of a X-ray diffraction peak, the average diameter of crystalline particles, and the diffraction angle respectively, and where λ=

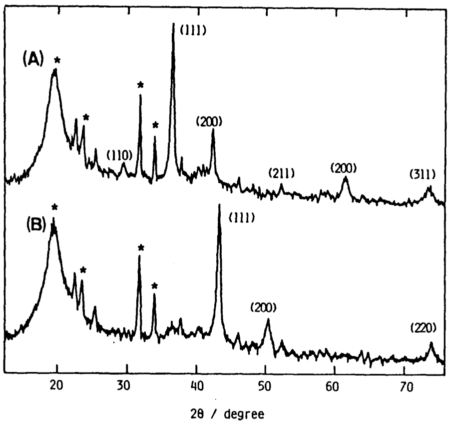

Fig. 1. X-Ray diffraction diagrams: (A) the reddish brown powder sample obtained from the hydrosol which was prepared by the reduction of Cu^{2+}-PVA complexes with hydrazine at R_r=[hydrazine]/[Cu^{2+}]=1; (B) the grayish black powder sample similarly obtained except at R_r=20 (the Cu^{2+}-PVA complexes were prepared at R_p=[PVA polymer residue]/[Cu^{2+}]=20). Peaks with asterisks are due to Na_2SO_4, and some peaks are marked with the Miller indices of Cu_2O crystals in (A) and Cu crystals in (B).

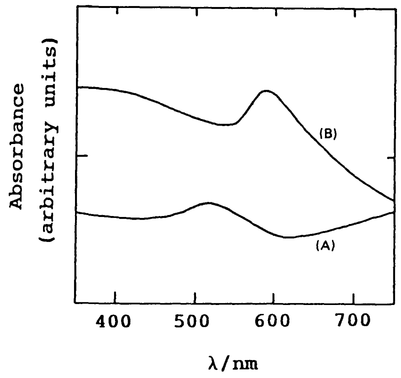

Fig. 2. Visible absorption spectra of the hydrosols corresponding to the (A) and (B) powder samples in Fig. 1.

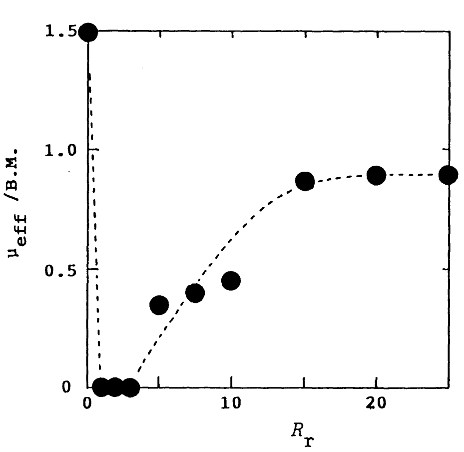

Fig. 3. A plot of the effective magnetic moment (μ_{eff}) against R_r for the powder samples obtained from hydrosols prepared at varying R_r values (see the caption of Fig. 1 as to R_r).

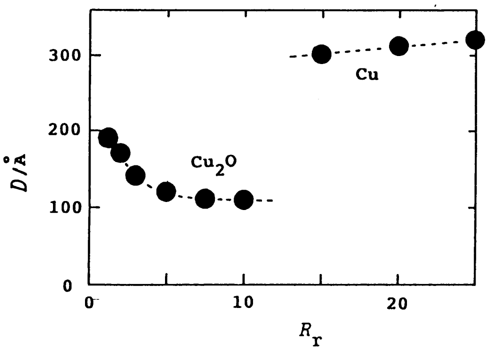

Fig. 4. A plot of the average diameters (D) of Cu_2O and Cu particles included in the powder samples against R_r (see the caption of Fig. 1 as to R_r).

1.54178 Å for Cu $K\alpha$ radiation. In this work, a strong X-ray diffraction peak for the (111) plane in every particle species was used for the purpose mentioned above. The results, summarized in Fig. 4, indicate that the average diameter of Cu particles in the grayish black samples of $R_r > 15$ are almost constantly about 300 Å, while that of Cu_2O particles in the reddish brown sample of $R_r = 1$ is about 200 Å. Further, there is a tendency for the diameter to decrease with the increase in R_r. We have a plan on hand for reinvestigating these particle sizes in the cast films of the present colloidal solutions by the use of a transmission electron microscope. It has been reported that the particle size of $Cu(OH)_2$ in the Cu^{2+}-PVA complexes may be extremely small, as small as less than 20 Å.[6] From this result and Fig. 4, it is concluded that there is a gathering process of small particles and, therefore, a growing process of particle size during the reductions of $Cu(OH)_2$ to Cu_2O and of Cu_2O to Cu by hydrazine in the presence of PVA, suggesting a reorganization in the interaction of such particles with PVA at every stage of reduction.

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